EAST Search History

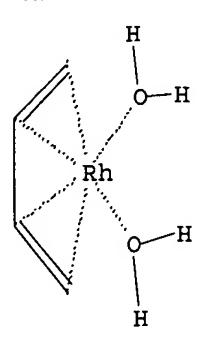
Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
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L2	2132	(502/152).CCLS.	US-PGPUB; USPAT; EPO; JPO	OR	OFF	2007/03/29 19:11
L3	1436	(502/155).CCLS.	US-PGPUB; USPAT; EPO; JPO	OR	OFF	2007/03/29 19:11

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(FILE 'HOME' ENTERED AT 15:51:20 ON 29 MAR 2007)

FILE 'REGISTRY' ENTERED AT 15:52:05 ON 29 MAR 2007 L1 STRUCTURE UPLOADED

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Structure attributes must be viewed using STN Express query preparation.

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SAMPLE SEARCH INITIATED 15:52:32 FILE 'REGISTRY'
SAMPLE SCREEN SEARCH COMPLETED - 7216 TO ITERATE

27.7% PROCESSED 2000 ITERATIONS INCOMPLETE SEARCH (SYSTEM LIMIT EXCEEDED) SEARCH TIME: 00.00.01

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FULL FILE PROJECTIONS: ONLINE **COMPLETE**

BATCH **COMPLETE**

PROJECTED ITERATIONS: 139228 TO 149412

PROJECTED ANSWERS: 0 TO 0

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100.0% PROCESSED 143880 ITERATIONS 28 ANSWERS SEARCH TIME: 00.00.01

L3 28 SEA SSS FUL L1

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COST IN U.S. DOLLARS
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=> s 13

L4 20 L3

=> d 1-20 bib abs

- L4 ANSWER 1 OF 20 CAPLUS COPYRIGHT 2007 ACS on STN
- AN 2006:855421 CAPLUS
- DN 145:419292
- TI Reactivity of [Cp*Rh(η6-C6H3NH2-2,6-i-Pr2)] (OTf)2 toward phosphines and alkynes
- AU Lim, Mi S.; Baeg, Ji Young; Lee, Soon W.
- CS Department of Chemistry (BK21), Institute of Basic Science, Sungkyunkwan University, Suwon, 440-746, S. Korea
- SO Journal of Organometallic Chemistry (2006), 691(19), 4100-4108 CODEN: JORCAI; ISSN: 0022-328X
- PB Elsevier Ltd.
- DT Journal
- LA English
- OS CASREACT 145:419292
- The cationic aniline complex [Cp*Rh(η6-2,6-(Me2CH)2C6H3NH2)] (OTf)2 (1) was prepared from either [Cp*Rh(η2-NO3)(η1-OTf)] or [Cp*Rh(OH2)3] (OTf)2 and 2,6-diisopropylaniline. Complex 1 underwent substitution with phosphines or phosphites, indicating the labile character of the η6-aniline ligand. Complex 1 mediated cycloaddn. reactions of several alkynes in refluxing ethanol: the [2 + 2] dimerization for Ph-C.tplbond.C-Ph and the [2 + 2 + 1] trimerization for PhC.tplbond.CH and p-CH3C6H4C.tplbond.CH. The unexpected cyclobutadiene complex [Cp*Rh(η4-C4(C(O)CH3)2H(SiMe3))] was obtained from complex 1 and Me3SiC.tplbond.C-C.tplbond.CSiMe3 and structurally characterized by x-ray diffraction.
- RE.CNT 39 THERE ARE 39 CITED REFERENCES AVAILABLE FOR THIS RECORD ALL CITATIONS AVAILABLE IN THE RE FORMAT
- L4 ANSWER 2 OF 20 CAPLUS COPYRIGHT 2007 ACS on STN
- AN 2005:373102 CAPLUS
- DN 143:275996
- TI Crystal structures of organometallic aqua complexes [Cp*RhIII(bpy)(OH2)]2+ and [Cp*RhIII(6,6'-Me2bpy)(OH2)]2+ used as key catalysts in regioselective reduction of NAD+ analogues
- AU Ogo, Seiji; Hayashi, Hideki; Uehara, Keiji; Fukuzumi, Shunichi
- CS Department of Material and Life Science, Graduate School of Engineering, Presto & Crest, Osaka University, Osaka, 565-0871, Japan
- SO Applied Organometallic Chemistry (2005), 19(5), 639-643 CODEN: AOCHEX; ISSN: 0268-2605
- PB John Wiley & Sons Ltd.
- DT Journal
- LA English
- Crystal structures of organometallic aqua complexes [Cp*RhIII(bpy)(OH2)]2+ $(1, Cp* = \eta 5-C5Me5, bpy = 2,2'-bipyridine)$ and [Cp*RhIII(6,6'-Me2bpy)(OH2)]2+ (2, 6,6'-Me2bpy = 6,6'-dimethyl-2,2'-bipyridine) used as

key catalysts in regioselective reduction of NAD+ analogs were determined by x-ray

anal. The yellow crystals of 1(PF6)2 and orange crystals of 2(CF3SO3)2 used in the x-ray anal. were obtained from aqueous solns. Crystals of 1(PF6)2 are monoclinic, space group P21/c, and crystals of 2(CF3SO3)2 are monoclinic, space group P21/n. The Rh-Oaqua length of 2.194(4) Å obtained for 1(PF6)2 is significantly different from that of 2.157(3) Å obtained for the previously reported disorder model [Cp*RhIII(bpy) (0.7H2O/0.3MeOH)] (CF3SO3)2·0.7H2O in which the coordinated H2O is replaced by a coordinated MeOH. The five-membered ring involving the Rh atom and the 6,6'-Me2bpy chelating unit in 2(CF3SO3)2 is not flat, whereas the five-membered chelate ring in 1(PF6)2 is nearly flat. Such a nonplanar structure in 2(CF3SO3)2 is ascribed to the steric repulsion between the 6,6'-Me2bpy ligand and the Cp* ligand.

RE.CNT 28 THERE ARE 28 CITED REFERENCES AVAILABLE FOR THIS RECORD ALL CITATIONS AVAILABLE IN THE RE FORMAT

- L4 ANSWER 3 OF 20 CAPLUS COPYRIGHT 2007 ACS on STN
- AN 2004:837023 CAPLUS
- DN 142:38364
- TI Azido- or hydroxyl-capped half-cubanes containing Cp*Rh fragments: $[Cp*3Rh3(\mu-X)3(\mu3-X)]2+(X-=OH-or N3-)$
- AU Han, Won Seok; Lee, Soon W.
- CS Department of Chemistry (BK21), Institute of Basic Science, Sungkyunkwan University, Suwon, 440-746, S. Korea
- SO Dalton Transactions (2004), (20), 3360-3364 CODEN: DTARAF; ISSN: 1477-9226
- PB Royal Society of Chemistry
- DT Journal
- LA English
- OS CASREACT 142:38364
- Trinuclear half-sandwich rhodium cubane-shaped ligand-bridged complexes were prepared and characterized. Treatment of [Cp*Rh(H2O)3](OTf)2 (1) with Me3SiNHCMe3 in acetone gave a hydroxyl-capped half-cubane [Cp*3Rh3(μ-OH)3(μ3-OH)](OTf)3(Me3CNH3) (2). Slow diffusion of Me3SiN3 in di-Et ether into compound 1 in acetone produced an azido-capped half-cubane [Cp*3Rh3(μ-N3)3(μ3-N3)](OTf)2 (3). On the other hand, treating 1 with Me3SiN3 in acetone gave an azido-bridged, dinuclear rhodium(III) complex [Cp*Rh(μ-N3)(OH2)]2(OTf)2 (4). Complexes 2 and 3 represent the first azido- or hydroxyl-capped, incomplete cubane-type Rh clusters. Under appropriate conditions, complexes 2 and 3 could be converted to complex 4. The structures of all products were determined by x-ray diffraction.
- RE.CNT 67 THERE ARE 67 CITED REFERENCES AVAILABLE FOR THIS RECORD ALL CITATIONS AVAILABLE IN THE RE FORMAT
- L4 ANSWER 4 OF 20 CAPLUS COPYRIGHT 2007 ACS on STN
- AN 2004:373424 CAPLUS
- DN 141:123740
- Various forms of linear dipyridyls in discrete rectangles, dinuclear rods, and one-dimensional networks containing (η5-pentamethylcyclopentadienyl)rhodium(III)
- AU Seok Han, Won; Lee, Soon W.
- CS Department of Chemistry (BK21), Institute of Basic Science, Sungkyunkwan University, Suwon, 440-746, S. Korea
- SO Dalton Transactions (2004), (10), 1656-1663 CODEN: DTARAF; ISSN: 1477-9226
- PB Royal Society of Chemistry
- DT Journal
- LA English
- OS CASREACT 141:123740
- AB [Cp*Rh(η 1-NO3)(η 2-NO3)] (1) reacted with pyrazine (pyz) to give dinuclear [Cp*Rh(η 1-NO3)(μ -pyz)0.5]2·CH2Cl2 (3·CH2Cl2). Tetranuclear rectangles [Cp*Rh(η 1, μ -X)(μ -

L)0.5]4(OTf)4 (4a: X = N3, L = bpy; 4b: X = N3, L = bpe; 4c: X = NCO, L = bpy) were prepared from [Cp*Rh(H2O)3](OTf)2 (2), a pseudo-halide (Me3SiN3 or Me3SiNCO), and a linear dipyridyl {4,4'-bipyridine (bpy) or trans-1,2-bis(4-pyridyl)ethylene (bpe)} by self-assembly through 1-pot synthesis at room temperature Treating complex 2 with NH4SCN and dipyridyl

gave

dinuclear rods, (LH2) [Cp*Rh(η1-SCN)3]2 (5a: L = bpy; 5b: L = bpe), in which two Cp*Rh(η1-SCN)3 units are connected by the diprotonated dipyridyl (LH22+) through N+-H···N H bonds.

Reactions of complex 2 with 1-(trimethylsilyl)imidazole (TMSIm) and dipyridyl (bpy or bpe) also produced another family of dinuclear rods [Cp*Rh(ImH)3]2·L (6a: L = bpy; 6b: L = bpe). Treating 1 and 2 with TMSIm and NH4SCN (in the absence of dipyridyl) generated a 1-dimensional chain [Cp*Rh(ImH)3](NO3)2 (7) and a 1-dimensional helix [Cp*Rh(η1-SCN)2(η1-SHCN)]·H2O (8·H2O), resp. The structures of complexes 3·CH2Cl2, 4a·H2O, 4c·2H2O, 5b, 6a, 7 and 8·H2O were determined by x-ray diffraction.

RE.CNT 47 THERE ARE 47 CITED REFERENCES AVAILABLE FOR THIS RECORD ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 5 OF 20 CAPLUS COPYRIGHT 2007 ACS on STN

AN 2003:461305 CAPLUS

DN 139:364914

Synthesis, NMR and properties of a novel crown ether dimer. X-ray molecular structure of bis(2,5-dimethoxy-4,6-dimethyl-1,3-xylyl)-18-crown-

AU Amouri, Hani; Besace, Yvon; Vaissermann, Jacqueline

CS Laboratoire de Chimie Inorganique et Materiaux Moleculaires, UMR 7071-CNRS, Universite Pierre-et-Marie-Curie, Paris, 75252, Fr.

SO Comptes Rendus Chimie (2003), 6(2), 193-197 CODEN: CRCOCR; ISSN: 1631-0748

PB Editions Scientifiques et Medicales Elsevier

DT Journal

LA English

OS CASREACT 139:364914

GI

Ι

The synthesis and complete characterization of the precursor 3,5-di(hydroxyethyloxymethyl)-2,6-dimethylhydroquinone-dimethylether and that of the crown ether I are reported. Further the X-ray structure of

this novel crown ether I is included, which provide us with valuable information about its solid-state structure [orthorhombic, Pbca, a 10.552(1), b 11.839(3), c 21.790(3)Å, α 90, β 90, γ 90°, V 2722.1(8) Å3, Z 4]. The title mol. I lies about a center of symmetry. Thus the novel 18-membered macrocycle I has a sym. configuration. Interestingly, a side view of the mol. shows that the two methoxy groups on each ring are on the same side, face to face and bend over the two arene units in the macrocycle. Finally, preliminary studies of its complexing property towards rhodium cations are presented and discussed.

RE.CNT 17 THERE ARE 17 CITED REFERENCES AVAILABLE FOR THIS RECORD ALL CITATIONS AVAILABLE IN THE RE FORMAT

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L4 ANSWER 6 OF 20 CAPLUS COPYRIGHT 2007 ACS on STN
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AN 2002:838969 CAPLUS

DN 138:195689

TI Excited state properties of aqueous (2'-deoxyadenosinato) - (pentamethylcyclopentadienyl)rhodium(III) cyclic trimer

AU Kunkely, Horst; Vogler, Arnd

CS Institut fur Anorganische Chemie, Universitat Regensburg, Regensburg, D-93040, Germany

SO Inorganica Chimica Acta (2002), 338, 265-267 CODEN: ICHAA3; ISSN: 0020-1693

PB Elsevier Science B.V.

DT Journal

LA English

The cyclic trimer [(C5Me5)RhIII(doa)]33+ with doa = 2'-deoxyadenosinate is characterized by a low-energy ligand field (LF) excited state which is emissive (λmax = 580 nm) and reactive. The irradiation of the complex in water leads to a photoaquation with the formation of [(C5Me5)RhIII(H2O)3]2+ and doaH.

RE.CNT 18 THERE ARE 18 CITED REFERENCES AVAILABLE FOR THIS RECORD ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 7 OF 20 CAPLUS COPYRIGHT 2007 ACS on STN

AN 2002:716518 CAPLUS

DN 137:228603

TI NAD(P) mimic for use in enzymic redox reactions

IN Fish, Richard H.; Kerr, John B.; Lo, Christine H.

PA The Regents of the University of California, USA

SO PCT Int. Appl., 63 pp. CODEN: PIXXD2

DT Patent

LA English

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			CY,	DE,	DK,	ES,	FI,	FR,	GB,	GR,	IE,	IT,	LU,	MC,	NL,	PT,	SE,	TR,
			BF,	ВJ,	CF,	CG,	CI,	CM,	GA,	GN,	GQ,	GW,	ML,	MR,	NE,	SN,	TD,	TG
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	EP	1373	552			A2		2004	0102]	EP 20	002-	7251	21		20	00203	311
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US 2003-729627 20031206 20041125

US 2004235084 **A1** 20010312 A PRAI US 2001-805726 WO 2002-US7444 20020311 CASREACT 137:228603; MARPAT 137:228603 os GI

Novel agents acting as co-factors for replacement of NAD(P)+/NAD(P)H AB co-enzyme systems in enzymic redox reactions are disclosed. A composition for replacement or regeneration of an NAD(P)+/NAD(P)H system in redox processes comprising (a) a polymer matrix, (b) a catalyst precursor, (3) a cofactor, and (d) an enzyme is further disclosed. The NAD(P) mimics are I [R = CN, CONH2, CONHMe, CSNH2, COCH3, COOMe; R1 = CH2(CH2O)nYR2,ribose-YR2, or (X substituted)benzyl; Y = OP(:0)0, OBO2, OSO2, NHMe, (CH2) nNH, adenine, imidazole; R2 = H, Me, (OCH2CH2) n, (NCH2CH2) n, [N:P(OMe)2]n; X = OMe, CF3, (OCH2CH2)n, OP(:O)OR3; R3 = H, Me, (OCH2CH2)n,(NCH2CH2)n, [N:P(OMe)2]n; n = 1-2000] and salts thereof. Thus, I with R1 = benzyl and R = various substituents such as CONH2 as well as I with R1 = ribose 5'-methylphosphate and R = CONH2 were synthesized and studied. Both of these coAlc. dehydrogenase enzyme mimics were used by horse liver alc. dehydrogenase to reduce phenethylmethylketone to the corresponding alc. with >93% ee (S-enantiomer). The reduced mimics were produced in this reaction using [Cp*Rh(bpy)(H2O)](OTf)2 as a catalyst precursor and sodium formate as hydride source.

ANSWER 8 OF 20 CAPLUS COPYRIGHT 2007 ACS on STN L4

AN 2001:817431 CAPLUS

DN136:98327

Bioorganometallic Chemistry. 13. Regioselective Reduction of NAD+ Models, TI 1-Benzylnicotinamide Triflate and β-Nicotinamide Ribose-5'-methyl Phosphate, with in Situ Generated [CpRh(Bpy)H]+: Structure-Activity Relationships, Kinetics, and Mechanistic Aspects in the Formation of the 1,4-NADH Derivatives

Lo, H. Christine; Leiva, Carmen; Buriez, Olivier; Kerr, John B.; Olmstead, AU Marilyn M.; Fish, Richard H.

Lawrence Berkeley National Laboratory, University of California, Berkeley, CS CA, 94720, USA

Inorganic Chemistry (2001), 40(26), 6705-6716 SO CODEN: INOCAJ; ISSN: 0020-1669

American Chemical Society PB

Journal DT

English LA

OS CASREACT 136:98327

Cofactor regeneration; i.e., regiospecific conversion of NAD+ to 1,4-NADH, ABhas been extensively studied and is a crucial component in the eventual use of 1,4-NADH in a variety of bioorg. synthesis processes involving the formation of chiral organic compds. We have studied the reduction of a model NAD+ compound, 1-benzylnicotinamide triflate, 1a, using [Cp*Rh(bpy)(H2O)]2+, 2 (Cp* = η 5-C5Me5, bpy = 2,2'-bipyridyl), as the catalyst precursor and sodium formate (HCO2Na) as the hydride source in 1:1 H2O/THF and have found exclusive 1-benzyl-1,4-dihydronicotinamide regioselectivity, as was observed previously for natural NAD+ that provided 1,4-NADH. Moreover, a variety of 3-substituted derivs. of 1-benzylpyridinium triflate, in addition

to the -C(O)NH2 group (1a), were also studied to ascertain that this 3-functionality (e.g., -C(0)NHCH3, -C(S)NH2, -C(O)CH3, -C(O)OCH3, and -CN, 1b,d-g) coordinates to a [Cp*Rh(bpy)H]+ complex to direct the concerted, regioselective transfer of the hydride group from the rhodium to the 4-ring position of the NAD+ model; all coordinating 3-substituents had relative rates in the 0.9-1.3 range with substrate 1a set to 1.0. If in fact the 3-substituent presented a steric effect [-C(O)NH(CH2CH3)2, 1c] or was a nonbinding group (-CH3, 1h; -H, 1i), no catalytic hydride transfer was observed even with the more electrophilic 2 and 6 ring positions being readily available, which further implicated the crucial coordination of the NAD+ model to the Cp*Rh metal ion center. We also found that the 1-benzyl substituent on the nitrogen atom exerted a substantial electron-withdrawing effect, in comparison to the electron-donating 1-Me substituent, and favorably affected the rate of the regioselective reduction (rate enhancement of 1-benzyl/1-Me = 2.0). The kinetics of the regioselective reduction of la were studied to show that the initial rate of reduction, ri, is affected by the concns. of the substrate, la, precatalyst, 2, and the hydride source, HCO2Na, in 1:1 H2O/THF: d[1-benzyl-1,4dihydronicotinamide]/dt = kcat[1a][2][HCO2Na]. Furthermore, we wish to demonstrate that a previously synthesized aqueous NAD+ model, β-nicotinamide ribose-5'-Me phosphate, 3, shows a similar regioselectivity for the 1,4-NADH analog, while the initial rate (ri) for the regioselective reduction of 3 and NAD+ itself was found to be comparable in water but faster by a factor of .apprx.3 in comparison to la in 1:1 H2O/THF; the solvent, THF, appeared to inhibit the rate of reduction in 1a by presumably competing with the substrate 1a for the Cp*Rh metal ion center. However, in H2O, the initial kinetic rate for substrate 3 was not affected by its concentration and implies that, in H2O, [Cp*Rh(bpy)H]+ formation is rate determining We assume that binding of 3 and NAD+ to the Cp*Rh metal ion center is also a pertinent step for 1,4-dihydro product formation, the exptl. rate expression in H2O being d[1,4-dihydro-β-nicotinamide ribose-5'-Me phosphate]/dt = kcat[2][HCO2Na]. What we have discovered, for the first time, is evidence that the regioselective reduction of NAD+ to 1,4-NADH by [Cp*Rh(bpy)H] + is a consequence of the amide's ability to coordinate to the Cp*Rh metal center, thereby constricting the kinetically favorable six-membered ring transition state for plausible concerted hydride transfer/insertion to C4 to regioselectively provide the 1,4-NADH derivative; [Cp*Rh(bpy)H] + can be categorized as a biomimetic enzymic hydride via its ability to bind and regioselectively transfer hydride to C4, exclusively. Clearly, the pyrophosphate and adenosine groups associated with the structure of NAD+ are not essential in the rate of hydride transfer to C4, with NAD+ model 3 having a similar initial rate (ri) of reduction as NAD+ itself in water. Finally, a catalytic cycle will be proposed to account for our overall observations.

RE.CNT 31 THERE ARE 31 CITED REFERENCES AVAILABLE FOR THIS RECORD ALL CITATIONS AVAILABLE IN THE RE FORMAT

- L4 ANSWER 9 OF 20 CAPLUS COPYRIGHT 2007 ACS on STN
- AN 1999:742293 CAPLUS
- DN 132:64390
- Bioorganometallic chemistry. Part 12. Reaction of [Cp*Rh(H2O)3] (OTf)2 with nicotinamide adenine dinucleotide in water: synthesis, structure, and a pH-dependent 1H-NMR and voltammetric study of the cyclic trimer product, [Cp*Rh(μ - η 1(N1): η 2(N6,N7)-9-(5'-ribose pyrophosphate-5''-ribose-1''-nicotinamide))adeninato]3(OTf)3
- AU Ogo, Seiji; Buriez, Olivier; Kerr, John B.; Fish, Richard H.
- CS Lawrence Berkeley National Laboratory, University of California, Berkeley, CA, 94720, USA
- SO Journal of Organometallic Chemistry (1999), 589(1), 66-74 CODEN: JORCAI; ISSN: 0022-328X
- PB Elsevier Science S.A.
- DT Journal
- LA English
- AB The reaction of [Cp*Rh(H2O)3](OTf)2 with nicotine adenine dinucleotide

(NAD+), an important co-factor in enzymic reactions, was studied using 1H-NMR spectroscopy, electrospray ionization mass spectroscopy (ESI/MS), cyclic voltammetry (CV), and isolation techniques, as a function of pH. The product was formulated from the above-mentioned spectroscopic data as the known Cp*Rh cyclic trimer structure, [Cp*Rh (μη1(N1):η2(N6,N7)-9-(5'-ribose pyrophosphate-5''-ribose-1''nicotinamide))adeninato]3(OTf)3, 3, which forms via a self-assembly mechanism as the pH is increased from 3 to 6 (1H-NMR). The authors also compared 3 with the putative one reported that formed via reaction with [(Cp*Rh)2(μ -Cl)2Cl2] and was tentatively assigned the formula, [Cp*Rh(NAD)Cl](Cl). In fact, both Cp*Rh synthons provide the same cyclic trimer product at pH 6, while a presumed mixture of [Cp*Rh(NAD)] and Cp*Rh aqua intermediates (at least eight Cp*Rh 1H-NMR signals are evident) were formed at 'pH 3.0. A full anal. of the CV data reveals that some Cp*Rh aqua complexes are electroactive at potentials around -1.2 V vs. Ag AgCl, but probably not the cyclic trimer, complex 3. Unfortunately, the authors were not able to use complex 3 in an intramol., regioselective reduction reaction, with Na formate as the hydride source, to provide the corresponding biol. active 1,4-dihydro derivative

RE.CNT 24 THERE ARE 24 CITED REFERENCES AVAILABLE FOR THIS RECORD ALL CITATIONS AVAILABLE IN THE RE FORMAT

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L4 ANSWER 10 OF 20 CAPLUS COPYRIGHT 2007 ACS on STN
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AN 1999:538977 CAPLUS

DN 131:299537

- TI Mechanistic Investigation on the Water Substitution in the η5-Organometallic Complexes Cp*Ir(H2O)32+ and Cp*Rh(H2O)32+
- AU Cayemittes, Sonia; Poth, Tilo; Fernandez, Maria J.; Lye, Peter G.; Becker, Michael; Elias, Horst; Merbach, Andre E.
- CS Institut de Chimie Minerale et Analytique, Universite de Lausanne BCH, Lausanne, CH-1015, Switz.
- SO Inorganic Chemistry (1999), 38(19), 4309-4316 CODEN: INOCAJ; ISSN: 0020-1669
- PB American Chemical Society

DT Journal

LA English

The substitution of H2O in the half-sandwich complexes Cp*Rh(H2O)32+ and Cp*Ir(H2O)32+ (Cp* = η 5-pentamethylcyclopentadienyl anion) by Cl-, Br-, I-, SCN-, py-CN (4-cyanopyridine), py-nia (nicotinamide), py (pyridine), TU (thiourea), and DMS (di-Me sulfide) was studied by stopped-flow spectroscopy at variable concentration, temperature, and pressure. The

proton dissociation consts. of the triaqua complexes, pKa = 6.47 (for Rh) and pKa = 3.86 (for Ir), as well as the equilibrium consts. for the formation of dinuclear $(Cp*M) 2 (\mu-OH) 3+$ were obtained by spectrophotometric titrns. The equilibrium consts. K1 for the formation of the monosubstituted complexes Cp*M(H2O)2L+/2+, as determined for anionic and neutral ligands L, lie in the range 102-105 M-1 and follow the sequences K(Cl-) < K(Br-) < K(I-) and K(py-CN) < K(py-nia) < K(py) < K(TU,DMS). Assuming the Eigen-Wilkins mechanism for the formation of the monosubstituted complexes, 2nd-order rate consts. kf,1 were corrected for outer sphere complex formation and for statistical factors to obtain rate constant ki' for the interchange step. The interchange rates ki' are nearly independent of the nature of L and very close to the rate of H2O exchange (kex(Rh) = (1.6 ± 0.3) + 105 s-1 and $kex(Ir) = (2.5 \pm 0.08) + 104 s-1)$. In all cases, i.e., for M = Rh and Ir and for L = anionic or neutral, the volume of the transition state is larger than that of the triaqua species. These findings support the operation of an Id mechanism without excluding a D mechanism. For a given ligand L, the substitution of another H2O mol. in the complexes Cp*M(H2O)2L+/2+ is by 1 order of magnitude slower than the substitution of the 1st H2O mol. in the triaqua species Cp*M(H2O)32+, as verified, for example, by kf,1 = 2.61 + 103 and kf,2 = 3.09 +102 M-1 s-1 for M = Ir and L = py.

RE.CNT 27 THERE ARE 27 CITED REFERENCES AVAILABLE FOR THIS RECORD

ALL CITATIONS AVAILABLE IN THE RE FORMAT

- L4 ANSWER 11 OF 20 CAPLUS COPYRIGHT 2007 ACS on STN
- AN 1999:303325 CAPLUS
- DN 131:181140
- TI Bio-organometallic chemistry: synthesis, structure, and molecular recognition chemistry of (η5-pentamethylcyclopentadienyl)rhodium-DNA/RNA complexes in water
- AU Fish, Richard H.
- CS Lawrence Berkeley National Laboratory, University of California, Berkeley, CA, 94720, USA
- SO Coordination Chemistry Reviews (1999), 185-186, 569-584 CODEN: CCHRAM; ISSN: 0010-8545
- PB Elsevier Science S.A.
- DT Journal; General Review
- LA English
- A review with 34 refs. A review of the aqueous bio-organometallic chemical of DNA/RNA nucleobases and of the co-factor, NAD, with an (n5-pentamethylcyclopentadienyl)rhodium aqua complex, [Cp*Rh(H2O)3] (OTf)2, at various pH values, will be presented. The unique structures of the Cp*Rh complexes with adenine, guanine, cytosine, thymine, and NAD bioligands were determined by a combination of 1H- and 31P-NMR, ESI/MS, and single crystal x-ray crystallog. Competitive reactivity studies, principally with the more reactive adenine and guanine derivs., showed the important bonding characteristics with these nucleobases, while a novel cyclic trimer structure with 9-substituted adenine derivs. provided a new supramol. receptor for mol. recognition studies with a variety of biol. important guests.
- RE.CNT 34 THERE ARE 34 CITED REFERENCES AVAILABLE FOR THIS RECORD ALL CITATIONS AVAILABLE IN THE RE FORMAT
- L4 ANSWER 12 OF 20 CAPLUS COPYRIGHT 2007 ACS on STN
- AN 1996:181971 CAPLUS
- DN 124:289838
- TI Aqueous Organometallic Chemistry. 2. 1H NMR Spectroscopic, Synthetic, and Structural Study of the Chemo- and Diastereoselective Reactions of [Cp*Rh(H2O)3]2+ with Nitrogen Ligands as a Function of pH
- AU Ogo, Seiji; Chen, b Hong; Olmstead, Marilyn M.; Fish, Richard H.
- CS Lawrence Berkeley National Laboratory, University of California, Berkeley, CA, 94720, USA
- SO Organometallics (1996), 15(8), 2009-13 CODEN: ORGND7; ISSN: 0276-7333
- PB American Chemical Society
- DT Journal
- LA English
- The reactions of a new Cp*Rh aqua synthon, [Cp*Rh(H2O)3]2+ (1), at acidic pH values (2-6) with aniline (2), pyridine (3), and L-phenylalanine (4) have provided interesting chemo- and diastereoselectivities as studied by 1H NMR, FAB/MS, and single-crystal x-ray crystallog. The reaction of 2 and aqua complex 1, at pH values from 4 to 6, quant. provided [Cp*Rh(η6-aniline)]2+ (5); the structure of 5 was unequivocally determined by a single-crystal x-ray anal., which also showed an approx. 25% η5 component. Compound 3 reacted with 1, at pH 2-6, to selectively provide [Cp*Rh(η1-pyridine)n(H2O)3-n]2+ (n = 1-3) complexes 6a-c as a function of pH. Surprisingly, complex 1 reacted with 4, from pH 4 to 6, to provide only one diastereomer of the known cyclic trimer [(Cp*Rh)(μ-η1-(OCO):η2-(N,OCO)-L-phenylalanine)]33+ (7; SC,SC,SC,SRh,SRh,SRh), an example of a one-step, highly diastereoselective reaction in H2O.
- L4 ANSWER 13 OF 20 CAPLUS COPYRIGHT 2007 ACS on STN
- AN 1995:805163 CAPLUS
- DN 124:29993
- TI Organometallic aqua complexes. Part 3. Olefin aqua complexes of rhodium(I)
- AU Koelle, Ulrich; Goerissen, Ralf; Wagner, Trixie

- CS Inst. Inorganic Chem., Aachen Technical Univ., Aachen, D-52074, Germany
- SO Chemische Berichte (1995), 128(9), 911-17 CODEN: CHBEAM; ISSN: 0009-2940
- PB VCH
- DT Journal
- LA English
- OS CASREACT 124:29993
- Dehalogenation of halide precursors [(olefin)RhCl]2 [olefin = ethylene, 1,5-cyclooctadiene (COD), norbornadiene (NBD), 2,3-dimethylbutadiene (DMB)] in water gave the corresponding cis-diolefin aqua ions. Attempted isolation of [(COD)Rh(H2O)2]OTS yielded crystals of (COD)Rh(H2O)(η1-OTS), the structure of which was determined by x-ray crystallog. (space group P1, Z = 2, Rw = 0.030). [(NBD)Rh(H2O)2]SbF6 formed in solution upon dehalogenation of [(NBD)RhCl]2 with AgSbF6 in aqueous acetone, and decomposed upon attempted isolation into [(NBD)Rh(η6-toluene)]SbF6 10 and [(NBD)2Rh]SbF6 11 in the presence of adventitious toluene. The crystal structures of 10 (space group P21/n, Z = 8, Rw = 0.065) and 11 (space group C2/c, Z = 4, Rw = 0.049) were determined C2H4 exchange in [(C2H4)2Rh(H2O)2]+ is fast with k2 .apprx. 104-105 s-1·M-1. The rate constant for water exchange in [(COD)Rh(H2O)2]+ was estimated as 104 s-1 (ΔG173.thermod. ≈ 25 kJ/mol) at 173 K.
- L4 ANSWER 14 OF 20 CAPLUS COPYRIGHT 2007 ACS on STN
- AN 1995:751140 CAPLUS
- DN 123:274256
- Bioorganometallic Chemistry. 7. A Novel, Linear, Two-Coordinate Rh(I) Anionic Amide Complex Formed by the Reaction of the Nucleobase, 1-Methylthymine, with the $[(Cp*Rh)2(\mu-OH)3]+$ Cation at pH 10: Molecular Recognition and Electrostatic Interaction within an Organometallic Hydrophobic Cavity
- AU Chen, Hong; Olmstead, Marilyn M.; Maestre, Marcos F.; Fish, Richard H.
- CS Lawrence Berkeley National Laboratory, University of California, Berkeley, CA, 94720, USA
- SO Journal of the American Chemical Society (1995), 117(35), 9097-8 CODEN: JACSAT; ISSN: 0002-7863
- PB American Chemical Society
- DT Journal
- LA English
- AB [Cp*Rh(H2O)3] (OTf)2 (Cp* = pentamethylcyclopentadienyl) reacted with 1-methylthymine (HL) to give a linear [LRhL] adduct with [(Cp*Rh)2(μ -OH)3]+. Crystal structure data are given for the adduct as a hydroxide salt hydrate. The mechanism for the reaction is discussed in terms of mol. recognition.
- L4 ANSWER 15 OF 20 CAPLUS COPYRIGHT 2007 ACS on STN
- AN 1995:578828 CAPLUS
- DN 123:112355
- TI Aqueous Organometallic Chemistry: Structure and Dynamics in the Formation of $(\eta 5\text{-Pentamethylcyclopentadienyl})$ rhodium Aqua Complexes as a Function of pH
- AU Eisen, Moris S.; Haskel, Ariel; Chen, Hong; Olmstead, Marilyn M.; Smith, David P.; Maestre, Marcos F.; Fish, Richard H.
- CS Lawrence Berkeley Laboratory, University of California, Berkeley, CA, 94720, USA
- SO Organometallics (1995), 14(6), 2806-12 CODEN: ORGND7; ISSN: 0276-7333
- PB American Chemical Society
- DT Journal
- LA English
- The structures of the (η5-pentamethylcyclopentadienyl)rhodium aqua complexes, as a function of pH, were studied by 1H, 13C, 17O, and 2-dimensional NOESY NMR spectroscopic techniques as well as by FAB mass spectrometry and potentiometric titration. The starting complex for the authors' NMR expts., [Cp*Rh(H2O)3](OTf)2, 1, was structurally

characterized by single-crystal x-ray crystallog. [130 K, Mo Ka radiation, $\lambda = 0.710.73 \text{ Å}$, a 23.979(9), b 9.726(4), c 18.257(6) \dot{A} , Z = 8, orthorhombic, space group Pna21, 3879 independent reflections, R = 0.0482, Rw = 0.1062]. Both 1H and 13C NMR titration expts. of the starting complex, 1, were performed by dissolving 1 in H2O (D2O) and obtaining spectra from pH 2-14. From pH 2-5 only one Cp* signal (1H NMR, 1.57 ppm; 13C NMR, 5.78 ppm) was observed, which was attributed to 1. As the pH of the solution with 1 was increased from 5 to 7, a dynamic and rapid equilibrium provides putative [Cp*Rh(μ-OH)(H2O)]2(OTf)2, 2, and [(Cp*Rh)2(μ -OH)3](OTf/OH), 3; unfortunately, only one 1H or 13C NMR signal for Cp*Rh at 1.50 (Cp*) or 5.41 ppm (C-Me), resp., was found for the latter two species, with broadening of the signals at pH 5.5-6, indicating that conversion from putative 2 to 3 was very fast on the NMR time scale. As the pH was further increased from 7 to 10, only the 1H or 13C NMR signal for 3 was observed at 1.50 or 5.41 ppm, resp. Starting the equilibrium from 3 (3 .dblharw. 1 via putative 2) within the pH range 14-2 provided similar results. The 2-dimensional NOESY NMR exchange phasing expts. at pH 5.8 and 11 showed correlations between the Cp* Me groups and the H2O or μ -OH groups attached to Rh and between both Cp* Me groups of the Cp*Rh aqua complexes, although sep. signals for bulk H2O and μ -OH or H2O ligands bonded to Rh were not observed due to a rapid exchange process. A potentiometric titration study gave further evidence that the conversion of $1 \rightarrow 3$ via putative 2 occurs rapidly with only one pKa of 5.3 being observed, reaffirming the fact that the conversion of 1 > 3 via putative 2 was extremely fast. The pseudo-first-order rate of conversion of $1 \rightarrow 3$ at pH 5.8 was measured by an NMR spin population transfer technique to be k1 = 7.18 s-1 (1, 0.034M; T1 = 1.6 s),while k-1, $3 \rightarrow 1$, is 2.93 s-1 (T1 = 1.5 s). The equilibrium constant, Ke. 170 NMR studies again showed that H20 mols. bonded to Cp*Rh and those in the bulk solution are in very fast exchange (k > 8150 s-1).

- L4 ANSWER 16 OF 20 CAPLUS COPYRIGHT 2007 ACS on STN
- AN 1995:491693 CAPLUS
- DN 123:83668
- TI Intrazeolite organometallics. Pentamethylcyclopentadienyl rhodium complexes
- AU Balkus, Kenneth J., Jr.; Nowinska, Krystyna
- CS Dep. Chem., univ. Texas Dallas, Richardson, TX, 75083-0688, USA
- SO Microporous Materials (1995), 3(6), 665-86 CODEN: MCMTEV; ISSN: 0927-6513
- PB Elsevier
- DT Journal
- LA English
- The incorporation of Cp* [Cp* = η 5-Me5C5] complexes of Rh in Y-type zeolites was studied. The preparation and characterization of intrazeolite complexes derived from (Cp*RhCl)2(μ -Cl)2 (1) and Cp*Rh(S)32+ (3) (S = H2O and CH2Cl2) are described. The reactivity of the Rh complexes with CO was followed by IR spectroscopy. The nature of the CO adducts is dependent on the type of charge-balancing cation. Intrazeolite complexes were characterized in H+, Li+, Na+ and Cs+ partially exchanged forms of zeolite Y. Addnl., the reaction of free Cp* ligand with intrazeolite Rh(I) dicarbonyl species is described.
- L4 ANSWER 17 OF 20 CAPLUS COPYRIGHT 2007 ACS on STN
- AN 1995:267241 CAPLUS
- DN 122:81590
- π -Arene Aqua Complexes of Cobalt, Rhodium, Iridium, and Ruthenium: Preparation, Structure, and Kinetics of Water Exchange and Water Substitution
- AU Dadci, Lynda; Elias, Horst; Frey, Urban; Hoernig, Andreas; Koelle, Ulrich; Merbach, Andre E.; Paulus, Helmut; Schneider, Jens Stefan
- CS Eduard-Zintl-Institut fuer Anorganische Chemie, Technische Hochschule Darmstadt, Darmstadt, D-64289, Germany
- SO Inorganic Chemistry (1995), 34(1), 306-15

CODEN: INOCAJ; ISSN: 0020-1669

PB American Chemical Society

DT Journal

LA English

The half-sandwich complexes [Cp*Co(bpy)(H2O)](PF6)2, [Cp*M(bpy)Cl]Cl (M = AB Rh, Ir), [L2-4Ru(bpy)Cl]Cl, and [Cp*Ir(OH)3IrCp*]OH·11H2O were prepared and characterized ($Cp* = L1 = \eta5$ -pentamethylcyclopentadienyl anion; bpy = 2,2'-bipyridine; L2 = η 6-benzene; L3 = η 6-cymene; L4 = n6-hexamethylbenzene). X-ray structure analyses of [CpRh(bpy)Cl]ClO4 (=C20H23Cl2N2O4Rh; orthorhombic, Pmn21; a = 12.720(5), b = 8.141(5), c = 10.504(5) Å; Z = 2; Rw = 0.0352), [Cp*Ir(bpy)Cl]ClO4 (=C20H23C12IrN2O4; orthorhombic, Pmn21; a = 12.714(4), b = 8.216(4), c =10.507(4) Å; Z = 2; Rw = 0.0235), and [Cp*Ir(OH)3IrCp*]OH·11H2O(=C20H56Ir2O15; orthorhombic, Pnma; a = 17.43(2), b = 17.93(2), c =10.52(1) \mathring{A} ; Z = 4; Rw = 0.0317) were carried out. Complexes [Cp*Rh(bpy)Cl]ClO4 and [Cp*Ir(bpy)Cl]ClO4 are isostructural. The dinuclear triply OH-bridged complex [Cp*Ir(OH)3IrCp*]OH·11H2O is isostructural with [Cp*Rh(OH)3RhCp*]OH·11H2O (Nutton et al. J. Chemical Society, Dalton Trans. 1981, 1997) with the two Cp* ligands being orientated in a coplanar fashion. The pKa's (298 K, I = 0.5 M (NaClO4)) of the coordinated water in the monoaqua species [Cp*M(bpy)(H2O)]2+ were 8.4 (Co), 8.2 (Rh), and 7.5 (Ir). The coordinated water in the species [L2-4Ru(bpy)(H2O)] 2+ is slightly more acidic (pKa = 6.9 (L2), 7.2 (L3), 7.3 (L4)). The vis absorption characteristics of the complex cations [Cp*M(bpy)X]2+/+ (M = Co, Rh, Ir) and [L2-4Ru(bpy)X]2+/+ are reported for X = H2O, SCN, I, Br, N3, thiourea, N-methylimidazole. Stopped-flow spectrophotometry was used to study the anation kinetics of the species $[Cp*M(bpy)(H2O)]_{2+}$ (M = Co, Rh, Ir) and $[L2-4Rh(bpy)(H2O)]_{2+}$ in aqueous solution

at pH 4.8 for a variety of monodentate anionic and neutral ligands X at variable temperature The kinetics follow a second-order rate law, rate = kX[X][complex]. On the basis of the Eigen-Wilkins mechanism, the second-order rate consts. kX were corrected for outer-sphere complex formation to obtain the rate consts. for the interchange step, ki, according to ki = kX/Kos (Kos was calculated). Rate consts. ki are nearly independent of the nature of the entering ligand X. The data for ki(average) (=mean of ki for all of the nucleophiles X studied) thus obtained range from ki(average) = 0.068 ± 0.038 s-1 for [L2Ru(bpy)(H2O)]2+ to ki(average) = 1590 ± 760 s-1 for [Cp*Rh(bpy)(H2O)]2+. For the homologous series [Cp*M(bpy)(H2O)]2+ (M = Co, Rh, Ir) the order for ki(average) (s-1) is Co:Rh:Ir = 0.60p1590:219 at 293 K. The data obtained for ki(average) can be taken as a good approximation

for

the rate of water exchange; i.e., ki(average) = kex. 170-NMR techniques were used to study the water exchange in [Cp*Rh(H2O)3]2+ and [Cp*Ir(H2O)3]2+ at variable temperature and pressure. The kinetic data for kex298 (s-1), Δ H.thermod. (kJ mol-1), Δ S.thermod. (J K-1 mol-1), and Δ V.thermod. (cm3 mol-1) are 1.6 + 105, 65.6, +75.3, and +0.6 for [Cp*Rh(H2O)3]2+ and 2.53 + 104, 54.9, +23.6, and +2.4 for [Cp*Ir(H2O)3]2+. The ratio kex(Rh)/kex(Ir) for the species [Cp+M(H2O)3]2+ is very close to the ratio ki(average)(Rh)/ki(average)(Ir) for the species [Cp*M(bpy)(H2O)]2+. The kinetic findings support the operation of an (dissociative) interchange mechanism (I(d)) for the anation of the species [LM(bpy)(H2O)]2+ (M = Co, Rh, Ir; L = L1-L4) as well as for the water exchange in [Cp*M(H2O)3]2+ (M = Rh, Ir). The rate-enhancing effect of π -arene ligands L on the water exchange in the half-sandwich cations [LM(H2O)3]2+ and [LM(bpy)(H2O)]2+ is discussed.

L4 ANSWER 18 OF 20 CAPLUS COPYRIGHT 2007 ACS on STN

AN 1993:626320 CAPLUS

DN 119:226320

TI Bioorganometallic chemistry. 3. Role of the phosphate group during reactions of adenosine monophosphate derivatives with an (η5-pentamethylcyclopentadienyl)rhodium aqua complex in the diastereoselective formation of cyclic trimers, [Cp*Rh(AMP)]3

AU Smith, David P.; Kohen, Elizabeth; Maestre, Marcos F.; Fish, Richard H. CS Lawrence Berkeley Lab., Univ. California, Berkeley, CA, 94720, USA

SO Inorganic Chemistry (1993), 32(19), 4119-22

CODEN: INOCAJ; ISSN: 0020-1669

DT Journal LA English

GI

The reactions of 5'-AMP in water (pH 5-8) with a $(\eta 5-$ AB pentamethylcyclopentadienyl)rhodium aqua complex, [Cp*Rh(H2O)2(OTf)2]x (1), showed, by 1H and 31P NMR spectroscopy, that the 5'-P(O)2:O group significantly inhibited cyclic trimer formation, [Cp*Rh[μ- $\eta 1(N1):\eta 2(N6,N7)-5'-AMP]]3$, via competition with N1 and NH6 for the Cp*Rh site and, as well, provided other mononuclear and dinuclear Cp*Rh-O-P complexes. In contrast, both the phosphate Me ester of 5'-AMP and 3'-AMP formed the cyclic trimer structures [Cp*Rh[μ - $\eta 1(N1):\eta 2(N6,N7)-methyl-5'-/3'-AMP)]3$ (e.g., I for 5'-AMP Me ester). The consequence of steric effects, as demonstrated by the position and substitution of the phosphate group attached to the ribose, on the diastereoselectivity of cyclic trimer formation, as observed by 1H and 31P NMR spectroscopy and CD anal. over time, shows that the phosphate Me ester of 5'-AMP provides a greater diastereoselectivity (6:1) after 1 wk of equilibration compared to 5'-AMP (1.5:1) and 3'-AMP (1.2:1).

L4 ANSWER 19 OF 20 CAPLUS COPYRIGHT 2007 ACS on STN

AN 1993:213274 CAPLUS

DN 118:213274

Bioorganometallic chemistry. 2. Synthesis and structural studies of the reactions of a nucleobase 1-methylcytosine with a $(\eta 5-$ pentamethylcyclopentadienyl)rhodium aqua complex

AU Smith, David P.; Olmstead, Marilyn M.; Noll, Bruce C.; Maestre, Marcos F.; Fish, Richard H.

CS Lawrence Berkeley Lab., Univ. California, Berkeley, CA, 94720, USA

SO Organometallics (1993), 12(3), 593-6 CODEN: ORGND7; ISSN: 0276-7333

DT Journal

English LA The reactions of a nucleobase, 1-methylcytosine (MC), with a Cp*Rh (Cp* = AB η5-pentamethylcyclopentadienyl) aqua complex, [(η5-Cp*)Rh(H2O)2)OTf)2]x (2, Tf = CF3SO2), provided two different complexes depending on the solvent media. Complex 3, $[(\eta 5-Cp*)Rh(\eta 1(N3)-$ MC) (η2 (O2, N3) -MC)] (OTf) 2, was formed when acetone was used as the solvent; however, when complex 3 was recrystd. from water (pH 5.1) or when water was used as the reaction solvent, complex 4, trans-[(η5-Cp*)Rh(η 1(N3)-MC)(μ -OH)]2(OTf)2, was isolated as a crystalline solid. The structures of 3 and 4 were verified by 1H NMR, FAB/MS, elemental anal., and single-crystal x-ray anal. The structure of complex 3 showed one MC ligand bound via N3 and the other chelated via N3 and C:O2. Inspection of several bond lengths of complex 4 indicates extensive intramol. hydrogen bonding of the μ -OH groups with the exocyclic NH2 and the 2-C:0 group. ANSWER 20 OF 20 CAPLUS COPYRIGHT 2007 ACS on STN L4AN 1991:207457 CAPLUS 114:207457 DN Preparation and redox behavior of a series of mixed ligand Cp*/aqua/tripod TIcomplexes of cobalt, rhodium and ruthenium Koelle, Ulrich; Klaeui, Wolfgang AU Inst. Anorg. Chem., Tech. Hochsch. Aachen, Aachen, D-5100, Germany CS Zeitschrift fuer Naturforschung, B: Chemical Sciences (1991), 46(1), SO 75-83 CODEN: ZNBSEN; ISSN: 0932-0776 Journal \mathtt{DT} LAGerman $[MLL']n+[M = Co, Rh, Ru; L, L' = \eta5-C5Me5, \eta5-C5Me5; L, L' =$ AB $\eta 5-C5Me5$, H2O; L, L' = $\eta 5-C5Me5$, tripod [CpCo[P(O)(OEt)2]3]; L, L' = tripod, tripod] were prepared Redox transitions of the complexes were investigated by cyclic voltammetry. The results are discussed in terms of ligand field and ligand charge stabilization of electron configurations. => s rhodium and diene and aquo 71441 RHODIUM 68987 DIENE 4146 AQUO 1 RHODIUM AND DIENE AND AQUO Li5 => d bib abs ANSWER 1 OF 1 CAPLUS COPYRIGHT 2007 ACS on STN L5 CAPLUS AN 2005:216735 142:267484 DN Diene-bis-aquo-rhodium(I) complexes, process TI for preparing them and their use Rivas-Nass, Andreas; Peter, Gerhard; Widmer, Juergen IN Umicore AG & Co. KG, Germany; Briel, Oliver; Karch, Ralf PA SO PCT Int. Appl., 15 pp. CODEN: PIXXD2 DTPatent

English LA FAN.CNT 1 APPLICATION NO. DATE DATE PATENT NO. KIND _ - - -20040810 WO 2004-EP8964 A2 ' 20050310 ΡI WO 2005021153 **A3** 20050512 WO 2005021153 WO 2005021153 20050707 B1 W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI,

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NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY,
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            AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK,
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             SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE,
            SN, TD, TG
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             IE, SI, FI, RO, CY, TR, BG, CZ, EE, HU, PL, SK
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OS.
    Diene-bis-aquo-rhodium(I) complex of the
AB
    general formula [Rh(diene)(H2O)2]X where diene is a
    cyclic diene and X is a noncoordinating anion is prepd, with
    applications in catalysis.
=> s rhodium and cod and aquo
         71441 RHODIUM
         47758 COD
         4146 AQUO
             O RHODIUM AND COD AND AQUO
L6
=> s rhodium and cod and water
         71441 RHODIUM
         47758 COD
       2512527 WATER
           122 RHODIUM AND COD AND WATER
L7
=> s 17 and "bis-aquo"
        490391 "BIS"
          4146 "AQUO"
            36 "BIS-AQUO"
                 ("BIS"(W)"AQUO")
L8
             0 L7 AND "BIS-AQUO"
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=> s l1 and rhodium

71441 RHODIUM

L2 8 L1 AND RHODIUM

=> d 1-8 bib abs

L2 ANSWER 1 OF 8 CAPLUS COPYRIGHT 2007 ACS on STN

AN 2006:1181513 CAPLUS

DN 146:122115

TI Tris(pyrazolyl)borate carbosilane dendrimers and metallodendrimers

AU Camerano, Jose A.; Casado, Miguel A.; Ciriano, Miguel A.; Oro, Luis A.

CS Departamento de Quimica Inorganica, Instituto de Ciencia de Mteriales de Aragon, C.S.I.C.-Universidad de Zaragoza, Zaragoza, E-50009, Spain

SO Dalton Transactions (2006), (44), 5287-5293 CODEN: DTARAF; ISSN: 1477-9226

PB Royal Society of Chemistry

DT Journal

LA English

Carbosilane-core tris-pyrazolylborate dendrimers and their rhodium AB and ruthenium alkene complexes were prepared by hydrosilylation of allylsilanes with dendritic hydrosilanes followed by dendritic hydrosilylation of potassium allyltris(isopropoxy)borate; the ligand dendrimers were then complexed with Rh and/or Ir precursors. Reaction of triisopropylborate with allylmagnesium bromide and further treatment with benzoyl chloride gave CH2:CHCH2B(OiPr)2 (1), which was then reacted with potassium pyrazolate and pyrazole to give the compound K[CH2 = CHCH2Bpz3] (2). The new allyl-containing scorpionate anion of 2 acts as a bi- or tri-dentate ligand, as shown by the mononuclear complexes [CH2:CHCH2Bpz3M(LL)] [M = Rh; 3 LL = nbd, 4 LL = tfb (tetrafluorobenzobarrelene), 5 LL = (CO)(PPh3); M = Ir; 6 LL = cod], obtained from reactions of the chloride-bridged dinuclear complexes $[M(\mu-Cl)(LL)]$ 2 with 2. Furthermore, the borate 1 represents a key material to achieve the attachment of tris(pyrazolyl)borate groups to the

peripheries of carbosilane dendrimers. Thus, the platinum-catalyzed hydrosilylation reactions of compound 1 with the dendritic cores Si[(CH2)3SiMe2H]4 (G(0)-(SiH)4), (G(1)-(SiH)8), and (G(2)-(SiH)16) gave the corresponding borate-containing dendrimers Si[(CH2)3SiMe2(CH2)3B(OiPr)2]4 (G(0)-B4), $Si[(CH2)3SiMe{(CH2)3SiMe2(CH2)3B(OiPr)2}2]4$ (G(1)-B8), and Si[(CH2)3SiMe{(CH2)3SiMe[(CH2)3SiMe2(CH2)3B(OiPr)2]2}2]4 (G(2)-B16) selectively in the anti-Markovnikov direction. Further reactions of G(0)-B4, G(1)-B8 and G(2)-B16 with potassium pyrazolate and pyrazole rendered the corresponding polyanionic dendrimers $K4[Si{(CH2)3SiMe2(CH2)3Bpz3}4]$ (G(0)-(Bpz3)4), G(1)-(Bpz3)8, and G(2)-(Bpz3)16, resp., which contain 4, 8, and 16 tris(pyrazolyl)borate groups sym. located around the dendritic peripheries. These unusual polyanionic dendrimers are excellent scaffolds to support metal centers, as shown by the reactions of G(0)-(Bpz3)4, G(1)-(Bpz3)8, and G(2)-(Bpz3)16 with $\{Rh(\mu-Cl)(nbd)\}$ 2] to give the neutral rhodadendrimers [Si{(CH2)3SiMe2(CH2)3Bpz3Rh(nbd)}4] G(0)-(Bpz3Rh)4, G(1)-(Bpz3Rh)8 and G(2)-(Bpz3Rh)16 as stable solids in excellent yields. Following this protocol, mixed rhodium/iridium metallodendrimers can be prepared THERE ARE 32 CITED REFERENCES AVAILABLE FOR THIS RECORD

RE.CNT 32 ALL CITATIONS AVAILABLE IN THE RE FORMAT

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ANSWER 2 OF 8 CAPLUS COPYRIGHT 2007 ACS on STN
L2
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2005:582102 CAPLUS AN

143:193619 DN

Cycloisomerization of Enynes via Rhodium Vinylidene-Mediated TI Catalysis

Kim, Hahn; Lee, Chulbom AU

Department of Chemistry, Princeton University, Princeton, NJ, 08544, USA CS

Journal of the American Chemical Society (2005), 127(29), 10180-10181 SO CODEN: JACSAT; ISSN: 0002-7863

American Chemical Society PΒ

Journal DT

English LA

OS CASREACT 143:193619

A novel rhodium-catalyzed cycloisomerization has been developed ABwhich converts various acyclic enynes to their cyclic diene isomers with endo-selectivity. Both [RhCl(COD)]2/P(4-FC6H4)3 and RhCl(PPh3)3 catalyst systems are effective in promoting the C-C bond-forming cyclization of enynes to furnish carbo- and heterocycles in good to excellent yield. Deuterium labeling studies suggest that the reaction proceeds through the formation of a rhodium vinylidene followed by subsequent [2 + 2] cycloaddn. with the alkene and ring-opening of the resulting rhodacyclobutane. These mechanistic studies reevaluate a previously proposed reaction pathway and lead to the discovery of a new cycloisomerization reaction that involves migration of silyl and selenyl substituents at the alkyne of enyne substrates upon cyclization.

THERE ARE 56 CITED REFERENCES AVAILABLE FOR THIS RECORD RE.CNT 56 ALL CITATIONS AVAILABLE IN THE RE FORMAT

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ANSWER 3 OF 8 CAPLUS COPYRIGHT 2007 ACS on STN
L2
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2005:216735 CAPLUS AN

142:267484 DN

Diene-bis-aquo-rhodium(I) complexes, process for preparing them TI and their use

Rivas-Nass, Andreas; Peter, Gerhard; Widmer, Juergen IN

Umicore AG & Co. KG, Germany; Briel, Oliver; Karch, Ralf PA

PCT Int. Appl., 15 pp. SO

CODEN: PIXXD2

Patent DT

English LA

FAN.CNT 1 APPLICATION NO. DATE DATE PATENT NO. KIND WO 2004-EP8964 WO 2005021153 A2 20040810 20050310 PΙ

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WO 2005021153
                          A3
                                20050512
     WO 2005021153
                          B1
                                20050707
         W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH,
             CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD,
             GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
             LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI,
             NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY,
             TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW
         RW: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM,
             AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK,
             EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE,
             SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE,
             SN, TD, TG
                                20050317
                                            DE 2003-10339790
    DE 10339790
                                                                    20030828
                          A1
                                20050310
                                            CA 2004-2536197
                                                                    20040810
     CA 2536197
                          A1
                                            EP 2004-763974
                                20060531
     EP 1660233
                          A2
                                                                    20040810
         R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT,
             IE, SI, FI, RO, CY, TR, BG, CZ, EE, HU, PL, SK
                                20061129
                                            CN 2004-80024756
     CN 1871067
                                                                    20040810
                          A
     JP 2007504104
                                            JP 2006-524271
                          T
                                20070301
                                                                    20040810
PRAI DE 2003-10339790
                                20030828
                          A
                                20040810
     WO 2004-EP8964
                          W
OS
     MARPAT 142:267484
     Diene-bis-aquo-rhodium(I) complex of the general formula
AB
     [Rh(diene)(H2O)2]X where diene is a cyclic diene and X
     is a noncoordinating anion is prepd, with applications in catalysis.
                            COPYRIGHT 2007 ACS on STN
     ANSWER 4 OF 8 CAPLUS
L2
AN
     2000:52124 CAPLUS
     132:180703
DN
     Asymmetric isomerisation of a cyclic diene: a
TI
     comparative study of BINAP and BIPNOR-rhodium(I) catalysts
     Faitg, Thomas; Soulie, Josette; Lallemand, Jean-Yves; Mercier, Francois;
AU
     Mathey, Francois
     Laboratoire de Synthese Organique, UMR 7652 CNRS, DCSO, Ecole
CS
     Polytechnique, Palaiseau, 91128, Fr.
     Tetrahedron (1999), Volume Date 2000, 56(1), 101-104
SO
     CODEN: TETRAB; ISSN: 0040-4020
     Elsevier Science Ltd.
PB
     Journal
\mathtt{DT}
     English
LA
     CASREACT 132:180703
OS
     The asym. isomerization of 5,7-dibenzyloxy-6-(trialkylsiloxy)cyclohepta-
AB
     1,3-diene to the corresponding 1,6-dibenzyloxy-7-
     (trialkylsiloxy)cyclohepta-1,3-diene can be accomplished at 90° in
     a 75/25 mixture of toluene and DME in the presence of a [Rh(BIPNOR)(cod)]+
     catalyst with 92% ee. A much lower ee is observed with BINAP.
     cases, the observed ee's increase with temperature A mechanism involving an
     η5-pentadienyl-Rh complex is proposed.
              THERE ARE 12 CITED REFERENCES AVAILABLE FOR THIS RECORD
RE.CNT 12
              ALL CITATIONS AVAILABLE IN THE RE FORMAT
     ANSWER 5 OF 8 CAPLUS COPYRIGHT 2007 ACS on STN
L2
     1998:307263 CAPLUS
AN
     129:40979
DN
     Preparation of ethane derivatives by catalytic hydrogenation of olefins
TI
     using tertiary phosphine complexes
     Tamao, Kohei; Saito, Seiki; Yamaguchi, Shigehiro; Yanagawa, Masao; Ota,
IN
     Yoshiaki
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Sumitomo Chemical Co., Ltd., Japan

Jpn. Kokai Tokkyo Koho, 13 pp.

CODEN: JKXXAF

Patent

Japanese

PA

SO

DT

LA

FAN.CNT 1

PATENT NO. KIND DATE APPLICATION NO. DATE

PI JP 10130175 A 19980519 JP 1996-290086 19961031

PRAI JP 1996-290086

19961031

OS CASREACT 129:40979; MARPAT 129:40979

ACHR1CHR5R6 [A = COX [X = H, lower alkyl, OH, lower alkoxy, NR7R8 (R7, R8 AB = H, lower alkyl, or NR7R8 = cyclyl), NR9R110 (R9, R10 = H, lower alkyl, aryl, acyl)]; R4-R6 = H, CO2H, lower alkyl, lower cycloalkyl which may be substituted with lower alkoxy, OH, carboxy, alkoxycarbonyl, alkylcarbonyl, amido, or halo, aryl which may be substituted with lower alkoxy, lower alkyl, OH, or halo] are prepared by treatment of ACR1:CR5R6 with H in the presence of [MYpZ]qXr [M = transition metal; X = anion, tertiary amine; Y]= linear or cyclic diene compds.; Z = R1nR23-nSiOCH(CH2PR32)CH(CH2PR32)OSiR1nR33-n (R1-R3 = lower alkyl, lower cycloalkyl, Ph which may be substituted with halo, lower alkyl, lower alkoxy; n = 0-3); p = 0, 1; q, r = 1, 2]. Use of the catalysts provide high conversion and selectivity. A MeOH solution of phenylitaconic acid and Et3N was treated with a MeOH solution of [(1,5-cyclooctadiene)[(2R,3R)-2,3bis(tert-butyldimethylsiloxy)-1,4-bis(diphenylphosphino)butane] rhodium(I)] tetrafluoroborate (preparation given) at room temperature for 24 h to give 70% (S)-2-benzylsuccinic acid (9.7% e.e.).

- L2 ANSWER 6 OF 8 CAPLUS COPYRIGHT 2007 ACS on STN
- AN 1995:773007 CAPLUS

DN 123:230862

- TI Microwave-activated preparation of silicone foams, and compositions useful therein
- IN Lewis, Larry N.; Schultz, William N.; Levinson, Lionel M.; Sumpter, Chris A.; Stein, Judith
- PA General Electric Co., USA
- SO U.S., 5 pp.

CODEN: USXXAM

DT Patent

LA English

FAN.CNT 1
PATENT NO. KIND DATE APPLICATION NO. DATE
PI US 5438081 A 19950801 US 1994-325913 19941020

PRAI US 1994-325913

AB Silicone foams are prepared by microwave curing of a mixture of ≥1 siloxane having vinyl groups attached to Si; ≥1 H siloxane; a blowing agent comprising water and, preferably, ≥1 monohydroxy aliphatic compound, a cyclodextrin inclusion compound of a Pt group metal coordination complex (preferably with a cyclic diene) and a filler. The use of the inclusion compound as a catalyst increases the shelf life of the composition, whereupon curing and foaming occur together upon exposure to microwave radiation.

- L2 ANSWER 7 OF 8 CAPLUS COPYRIGHT 2007 ACS on STN
- AN 1980:567591 CAPLUS
- DN 93:167591
- TI Rhodium hydroformylation catalyst
- IN Zuech, Ernest A.
- PA Phillips Petroleum Co., USA
- SO U.S., 8 pp. Division of U.S. No. 3,956,177. CODEN: USXXAM
- DT Patent
- LA English
- FAN.CNT 2

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE		
ΡI	US 4195042	A	19800325	US 1976-663004	19760302		
	US 3956177	A	19760511	US 1973-376519	19730705		

PRAI US 1971-173689 A2 19710820 US 1973-376519 A3 19730705

Complexes of LnRhXm (X = Cl, Br, I; L = cyclic diene or cyclic triene; n = 1, 2; m = 1, 2; n + m = 2, 3) treated with hydrazine or metal hydrides and phosphites or phosphines were used as hydroformylation catalysts. Thus, π -1,5,9-cyclododecatrienylrhodium(III) dichloride with Na hydride and tri-1-naphthyl phosphite in THF gave a complex which was used to hydroformylate 1-hexene to 77.5% hexanal.

L2 ANSWER 8 OF 8 CAPLUS COPYRIGHT 2007 ACS on STN

AN 1976:437669 CAPLUS

DN 85:37669

TI Rhodium hydroformylation catalyst

IN Zuech, Ernest A.

PA Phillips Petroleum Co., USA

SO U.S., 7 pp. CODEN: USXXAM

DT Patent

LA English

FAN. CNT 2

DAM CIVI	CENT NO.	KIND	DATE	APPLICATION NO.	DATE	
PAI	ENI NO.		DAIL	APPLICAÇION NO.		
PI US	3956177	A	19760511	US 1973-376519	19730705	
US	4195042	A	19800325	US 1976-663004	19760302	
PRAI US	1971-173689	A2	19710820			
US	1973-376519	A3	19730705			

AB A Rh hydroformylation catalyst for olefins was prepared from an organorhodium halide containing a cyclic diene or triene group, hydrazine or a metal hydride, and a P-containing adjuvant. The catalyst was used for hydroformylation of 1-hexene to n-heptaldehyde, and propene to n-butyraldehyde. The catalytic Rh compound used in examples was π -cyclododeca-1,5,9-trienylrhodium(III) dichloride. The hydrides and hydrazine compound were NaH, Na borohydride, and hydrazine. The P compns. were tri- α -naphthyl phosphite and triphenyl phosphite.